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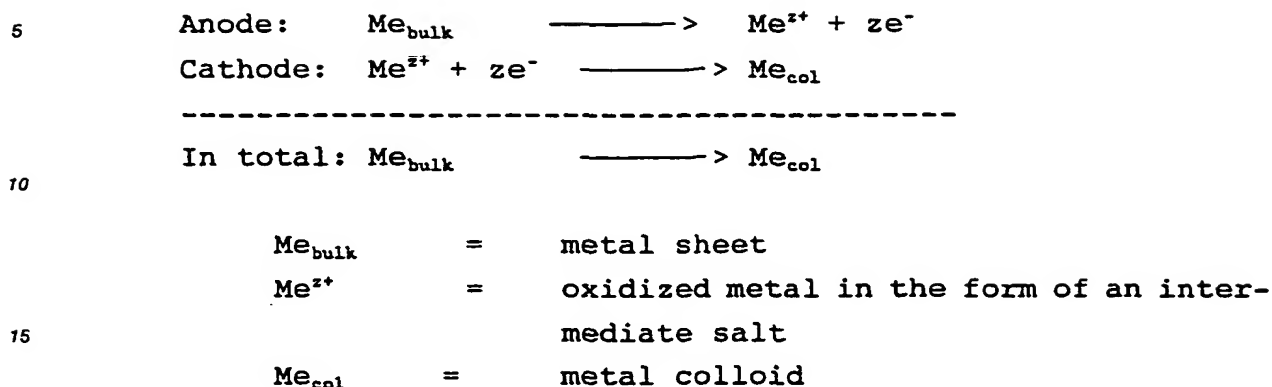
(54) **Electrochemical reduction of metal salts as a method of preparing highly dispersed metal colloids and substrate fixed metal clusters by electrochemical reduction of metal salts**

(57) The object of the invention is a method for the electrochemical preparation of metal colloids with particle sizes of less than 30 nm, characterized in that one or more metals of groups Ib, IIb, III, IV, V, VI, VIIb, VIII, lanthanoides, and/or actinoides of the periodic table are cathodically reduced in the presence of a stabilizer, optionally with a supporting electrolyte being added, in organic solvents or in solvent mixtures of organic solvents and/or water within a temperature range of between -78°C and +120°C to form metal colloidal solutions or redispersible metal colloid powders, optionally in the presence of inert substrates and/or soluble metal salts of the respective metals.

The invention further relates to soluble or redispersible colloids as well as application on substrates and immobilization thereof, in particular for the preparation of catalysts.

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Scheme 1.



As the supporting electrolyte and at the same time as a stabilizer for the colloids, quarternary ammonium or phosphonium salts $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+\text{X}^-$ and $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{P}^+\text{X}^-$, respectively, are suitable. A wide variety of combinations of R^1 , R^2 , R^3 and R^4 are possible. Examples include the symmetrical tetraalkylammonium salts with $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{n-butyl}$ or n-octyl , the mixed tetraalkylammonium salts with $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{methyl}$ and $\text{R}^4 = \text{cetyl}$, or chiral tetraalkylammonium salts having four different residues. Aryltrialkylammonium salts may also be used. Suitable counter ions include various anions, e.g. halogenides (Cl^- , Br^- , I^-), hexafluorophosphate (PF_6^-), carboxylates $\text{R}'\text{CO}_2^-$ ($\text{R}' = \text{alkyl, aryl}$), or sulfonates $\text{R}''\text{SO}_3^-$ ($\text{R}'' = \text{alkyl, aryl}$). A similar variety of phosphonium salts may be used, including tetraarylphosphonium salts, such as tetraphenylphosphonium bromide. Preferably, tetrabutylammonium chloride, bromide or hexafluorophosphate, tetraoctylammonium bromide, or tributylhexadecylphosphonium bromide are employed. As the metals, in particular transition metals, for example Fe, Co, Ni, Pd, Pt, Ir, Rh, Cu, Ag, or Au, are used. Suitable solvents are aprotic organic solvents, such as tetrahydrofuran (THF), toluene, acetonitrile (ACN), or mixtures thereof. The temperature in the electrolytic cell may be in the range between -78°C and $+120^\circ\text{C}$, preferably $15-30^\circ\text{C}$ or room temperature.

In this way, metal colloids of various metals and metal alloys having various sizes and being stabilized by quarternary ammonium or phosphonium salts can be synthesized. The size of the metal colloids is determined by varying the current density which immediately affects the reduction potential of the cathode. The higher the overvoltage, which is defined as the deviation of the reduction potential from the equilibrium potential, the smaller becomes the maximum size of the metal nuclei in the electrolytic boundary layer. These nuclei are trapped which is achieved by the fact that the surface-active agents used as supporting electrolytes form a protective shell around them and thus prevent further growth. Thus, the size of the metal colloids can be controlled. For instance, soluble Pd colloids stabilized by tetraoctylammonium bromide can be prepared with selected diameters of about 2 nm, 5 nm, or 10 nm, depending on the current density applied, i.e. 3.4, 1 and 0.4 mA/cm², respectively, at the same concentration of the stabilizer.

This method has the advantage that the $\text{R}_4\text{N}^+\text{X}^-$ stabilized metal colloids are formed without notable by-products and hence are readily isolated, that controlling of the particle size by adjusting the current density and/or the overpotential is possible, and that immobilization of the colloids by fixing them on substrates can easily be performed. Some metal sheets are more expensive than the respective metal salts; some metal sheets, especially in the case of metals very resistant to oxidation, cannot be dissolved at all anodically or only poorly so. From the redox potentials of the metals which can be found in tables in the relevant literature [*Handbook of Chemistry and Physics*, CRC Press, Boca Raton, Florida (USA), 1988], the latter behaviour can be understood. Metals such as for instance Pt or Rh can be anodically dissolved only conditionally in the described medium according to scheme 1. However, dissolution is a precondition for the above embodiment to succeed.

Another embodiment of an electrochemical method has now been found according to which metal salts are used and are reduced at the cathode to form stabilized clusters in the nanometer range. The invention will be successful even if metal salts are used whose corresponding metal sheet is readily dissolved anodically.

For performing the metal colloid synthesis of the invention according to said further embodiment, metal salts MX_n are used for electrochemical reduction, where quite different ligands X are suitable. In addition to

immobilized metal cluster is thus obtained in a simple manner. Alternatively, a slurry of the substrate in the electrolyte may be formed and electrolysis performed in the presence of the substrate. The metal clusters generated are fixed *in situ* on the substrate (e.g. coal). Further substrates that may be used are active charcoal, metal oxides (for instance SiO_2 , Al_2O_3 , MgO), or insoluble organic polymers (for example a polyamide, such as Kevlar®). The substrate may be doped with one or more metals, said doping being performed by classical methods or by the electrochemical process described herein. The particle size may conveniently be determined by transmission electron micrographs. It has been found that the metal colloids according to the present invention can be coated in particular on the surface of inert substrates like usual catalyst supports without penetration into the body of the support but providing in particular a monomolecular, bimolecular or multimolecular layer of the colloid with good adherence properties to the support surface.

The colloids prepared according to the invention can be used to apply metals in finely dispersed form on undoped or doped surfaces to form highly active heterogeneous catalysts. On the other hand, the colloids prepared according to the invention can be used as homogeneous catalysts. The substrate fixed metal clusters prepared according to the invention can be used as heterogeneous catalysts or as electrocatalysts in fuel cells. Thus, palladium colloids adsorbed on solid polymers or glasses serve as catalysts in electroless plating to metallize nonconductors. Another field of applications for the soluble colloids and substrate fixed metal clusters prepared according to the invention involves the development of novel materials having unusual electronic properties and providing important stimuli in the development of novel sensitive electronic components and very high scale integrated storage media based on quantum point arrays.

The colloids on undoped or doped substrates prepared according to the invention are highly active heterogeneous catalysts. They are useful e.g. as hydrogenation catalysts in hydrogenating olefins or aromatics. An application of technical interest is e.g. partial hydrogenation of benzene to form cyclohexene with substrate fixed ruthenium colloids or bimetallic colloids (e.g. Ru/Sn). The substrate fixed metal clusters prepared according to the invention may also be used as catalysts in Heck reactions, e.g. in the Pd-colloid catalyzed reaction of bromobenzene and styrene to form stilbene. The heterogeneous catalysts are also useful as electrocatalysts in fuel cells (in particular substrate fixed Pt and Pt/Ru clusters). The metal colloids prepared according to the invention are useful as homogeneous catalysts, which includes their use in two-phase systems (for instance H_2O /toluene), such as e.g. betaine stabilized Pd clusters soluble in H_2O . The soluble metal clusters may also be embedded in polymers to prepare materials for electronic, optical and magnetic applications. As the embedding component of those composite materials, there are used organic polymers, such as e.g. poly(p-phenylene-vinylene), poly(methyl methacrylate), polysilanes, and polystyrene, or inorganic polymers, such as zeolites, silicates, and metal oxides. The sol-gel process which is well-known in the art can be used to incorporate the metal clusters in amorphous metal oxide materials (e.g. SiO_2).

The soluble metal clusters can also be surface-deposited by electrophoretics to prepare novel materials for applications in optics and electronics, e.g. Pd on HOPG (highly oriented pyrolytic graphite).

To characterize the metal colloids, conventional analytical methods are used, in particular transmission electron microscopy (TEM) and elemental analysis. Another method of investigation that may be performed involves comparative studies by TEM/STM (scanning tunnel microscopy) which allow for a precise characterization of the stabilizing protective shell. The following examples illustrate the new method in detail without representing a limitation whatsoever thereof.

Example 1: (Pd)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 90 ml of 0.1 M tetraoctylammonium bromide in THF. Two sheets of pure palladium ($2 \times 2.5 \text{ cm}^2$ geometric electrode surface area, thickness 1 mm) at a distance of about 3 mm are used as the electrodes. All operations must be performed under an inert gas atmosphere (argon or nitrogen). With vigorous stirring by means of a magnetic stirrer, a current of 5 mA which is increased to 17 mA in the course of 20 minutes is passed between the palladium electrodes. By means of jacket cooling, the electrolytic cell is maintained at 16°C . In the course of the electrolysis, the electrolyte turns deep-black. After a charge of 640 C has been passed, the electrolysis is stopped and the electrolyte is pressed into a 150 ml nitrogenized vessel. During this period, 300 mg of Pd have dissolved anodically, corresponding to an anode efficiency of 90% with an uptake by palladium of 2 electrons. Addition of 30 ml of oxygen-free water to the electrolyte results in the formation of a brown-grey precipitate upon vigorous shaking. The latter is allowed to set for 24 hours whereupon the clear supernatant is syphoned off. Drying under oil pump vacuum for 20 minutes yields 411 mg (99% yield based on Pd

area, thickness 1 mm) at a distance of about 3 mm are used as the electrodes. Under ultrasonic action, a current of 1 mA which is increased to 2 mA in the course of 20 minutes is passed between the palladium electrodes. By means of jacket cooling, the electrolytic cell is maintained at 16°C. In the course of the electrolysis, the electrolyte turns deep-black. After 320 C have been passed, the electrolysis is stopped and the electrolyte is pressed into a 150 ml nitrogenized vessel. During this period, 140 mg of Pd have dissolved anodically, corresponding to a current efficiency of 85% with an uptake by palladium of 2 electrons. Addition of 20 ml of oxygen-free water to the electrolyte results in the formation of a brown-grey precipitate upon vigorous shaking. The latter is allowed to set for 24 hours whereupon the clear supernatant is syphoned off. After drying under oil pump vacuum for 20 minutes, 175 mg (99% yield based on Pd dissolved) of a grey-black powder is obtained. This powder readily dissolves in THF, acetone, toluene, DMF, and is insoluble in water, diethyl ether, acetonitrile, and pentane.

Elemental analysis: Pd: 74%

Mass spectrum: $m/z = 353$ (trioctylamine), 41 (ACN)

Transmission electron micrographs show a broader size distribution of colloids which are all ≤ 12 nm in diameter and in addition to spherically shaped colloids also include cornered ones. The course of the experiments in examples 1-4 will be absolutely analogous, if $\text{NMe}_2\text{dodecyl}_2\text{Br}$ or $\text{NMe}_2\text{octyl}_2\text{Br}$ is used as the supporting electrolyte.

Example 5: (Pd)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 90 ml of 0.05 M tetraoctylammonium bromide in ACN. All operations must be performed under an inert gas atmosphere (argon or nitrogen). Two sheets of pure palladium ($2 \times 2.5 \text{ cm}^2$ geometric electrode surface area, thickness 1 mm) at a distance of about 3 mm are used as the electrodes. Under ultrasonic action, a current of 5 mA which is increased to 20 mA in the course of 20 minutes is passed between the palladium electrodes. By means of jacket cooling, the electrolytic cell is maintained at 16°C. In the course of the electrolysis, the electrolyte turns deep-black. After 320 C have been passed, the electrolysis is stopped and the electrolyte is pressed into a 150 ml nitrogenized vessel. During this period, 156 mg of Pd have dissolved anodically, corresponding to a current efficiency of 95% with an uptake by palladium of 2 electrons. The electrolyte is allowed to stand for 24 hours during which a grey-brown to black precipitate is setting, and the clear supernatant is syphoned off. After drying under oil pump vacuum for 20 minutes, 205 mg (99% yield based on Pd dissolved) of a grey-black powder is obtained. This powder readily dissolves in THF, acetone, toluene, DMF, and is insoluble in water, diethyl ether, acetonitrile, and pentane. Elemental analysis: Pd: 74%.

Mass spectrum: $m/z = 353$ (trioctylamine), 41 (ACN)

Transmission electron micrographs show a narrow size distribution of colloids which are all ≤ 6 nm in diameter (maxima between 4-6 nm) and have spherical geometries.

Example 6: (Pd)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 90 ml of 0.0125 M tetraoctylammonium bromide in THF. All operations must be performed under an inert gas atmosphere. Two sheets of pure palladium ($2 \times 2.5 \text{ cm}^2$ geometric electrode surface area, thickness 1 mm) at a distance of about 3 mm are used as the electrodes. Under ultrasonic action, a current of 2 mA which is increased to 9 mA in the course of 20 minutes is passed between the palladium electrodes. By means of jacket cooling, the electrolytic cell is maintained at 16°C. In the course of the electrolysis, the electrolyte turns deep-black. After 160 C have been passed, the electrolysis is stopped and the electrolyte is pressed into a 150 ml nitrogenized vessel. During this period, 75 mg of Pd have dissolved anodically, corresponding to a current efficiency of 90% with an uptake by palladium of 2 electrons. Addition of 20 ml of oxygen-free water to the electrolyte results in the formation of a brown-grey precipitate upon vigorous shaking. The latter is allowed to set for 24 hours, whereupon the clear supernatant is syphoned off. After drying under oil pump vacuum for 20 minutes, 102 mg (99% yield based on Pd dissolved) of a grey-black powder is obtained. This powder readily dissolves in THF, acetone, toluene, DMF, and is insoluble in water, diethyl ether, acetonitrile, and pentane.

Elemental analysis: Pd: 74%

Mass spectrum: $m/z = 353$ (trioctylamine)

Transmission electron micrographs show a very broad size distribution of colloids which are in the range of 2-50 nm.

Transmission electron micrographs show a narrow size distribution of colloids which are all < 4 nm in diameter and have spherical geometries.

Example 10: (Pd)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 90 ml of 0.1 M tetrabutylammonium bromide in THF. All operations must be performed under an inert gas atmosphere (argon or nitrogen). Two sheets of pure palladium (2 x 2.5 cm² geometric electrode surface area, thickness 1 mm) at a distance of about 3 mm are used as the electrodes. With vigorous stirring by means of a magnetic stirrer, a current of 5 mA which is increased to 12 mA in the course of 20 minutes is passed between the palladium electrodes. By means of jacket cooling, the electrolytic cell is maintained at 28 °C. In the course of the electrolysis, the electrolyte turns deep-black. After 640 C have been passed, the electrolysis is stopped and the electrolyte is pressed into a 150 ml nitrogenized vessel. During this period, 308 mg of Pd have dissolved anodically, corresponding to a current efficiency of 93% with an uptake by palladium of 2 electrons. Addition of 10 ml of oxygen-free water to the electrolyte results in the formation of a brown-grey precipitate upon vigorous shaking. The latter is allowed to set for 24 hours, whereupon the clear supernatant is syphoned off. After drying under oil pump vacuum for 20 minutes, 350 mg (99% yield based on Pd dissolved) of a grey-black powder is obtained. This powder readily dissolves in DMF, and is insoluble in water, diethyl ether, THF, acetonitrile; and pentane.

Elemental analysis: Pd: 86.46%; C: 8.98%; H: 1.68%; N: 0.76%; Br: 2.06%. Mass spectrum: m/z = 242 (tetrabutylammonium); 185 (tributylamine). Transmission electron micrographs show a narrow size distribution of colloids which are all < 4 nm in diameter and have spherical geometries.

Electrolyses using NBu₄Cl, NBu₄I, and PBu₄Cl as stabilizers proceed in much the same manner.

Example 11: (Pd)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 90 ml of 0.1 M tetraoctylammonium bromide in THF. In this solution, 2.8 g of thoroughly dried and mortar-ground active charcoal is suspended. All operations must be performed under an inert gas atmosphere (argon or nitrogen). Two sheets of pure palladium (2 x 2.5 cm² geometric electrode surface area, thickness 1 mm) at a distance of about 3 mm are used as the electrodes. Under ultrasonic action, a current of 5 mA which is increased to 15 mA in the course of 20 minutes is passed between the palladium electrodes. By means of jacket cooling, the electrolytic cell is maintained at 16 °C. In the course of the electrolysis, the electrolyte turns deep-black. After 320 C have been passed, the electrolysis is stopped and the electrolyte is pressed into a 150 ml nitrogenized vessel. During this period, 155 mg of Pd have dissolved anodically, corresponding to a current efficiency of 93% with an uptake by palladium of 2 electrons. Further processing includes addition of 40 ml of ethanol and vigorous stirring. Filtering through a D4 frit and subsequent washing with 2 portions of 10 ml of ethanol and drying under oil pump vacuum yields 2.9 g of a grey-black powder. The catalyst thus obtained comprises 5.5% of Pd. Transmission electron micrographs show a narrow size distribution of Pd colloids in the range of 2 nm which are adsorbed on the active charcoal.

Example 12: (Ni)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 90 ml of 0.1 M tetraoctylammonium bromide in THF. Since the metal colloid is very sensitive to air and moisture, special care is to be taken that the solvents are free of water and oxygen. All operations must be performed under an inert gas atmosphere (argon or nitrogen). Two sheets of pure nickel (2 x 2.5 cm² geometric electrode surface area, thickness 1 mm) at a distance of about 3 mm are used as the electrodes. Under ultrasonic action, a current of 5 mA which is increased to 15 mA in the course of 20 minutes is passed between the Ni electrodes. By means of jacket cooling, the electrolytic cell is maintained at 16 °C. In the course of the electrolysis, the electrolyte turns deep-black. After 320 C have been passed, the electrolysis is stopped and the electrolyte is pressed into a 150 ml nitrogenized vessel. During this period, 89 mg of Ni have dissolved anodically, corresponding to a current efficiency of 96% with an uptake by nickel of 2 electrons. Evaporation of the solvent under oil pump vacuum yields 5 g of a black viscous mass. Addition of 30 ml of an ether/ethanol mixture (9/1) results in the formation of a grey-black precipitate upon vigorous shaking. The latter is allowed to set for 24 hours, whereupon the clear supernatant is syphoned off. Washing is performed with 10 ml of pentane, and after drying under oil pump vacuum for 20 minutes, 178 mg (80% yield based on Ni dissolved) of a grey-black powder is obtained which is amorphous by X-ray diffraction. This powder readily

pressed into a 150 ml nitrogenized vessel. During this period, 1300 mg of Au have dissolved anodically, corresponding to a current efficiency of 96% with an uptake by gold of 1 electron. Evaporation of the solvent under oil pump vacuum leaves 6.2 g of a black viscous mass. The colloid is sensitive to air and moisture. The colloid thus obtained is redispersible in THF. When the solution is too much diluted, a nanocrystalline Au powder precipitates which is amorphous by X-ray diffraction.

Elemental analysis of the colloid: 20% of Au

Elemental analysis of the powder: 97% of Au

Transmission electron micrographs show a narrow size distribution of colloids which are all < 12 nm in diameter and have spherical or angular geometries.

Example 16: (Ni)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 90 ml of 0.1 M tetraoctylammonium bromide in THF/ACN (4/1). Since the metal colloid is very sensitive to air and moisture, special care is to be taken that the solvents are free of water and oxygen. All operations must be performed under an inert gas atmosphere (argon or nitrogen). Two sheets of pure nickel ($2 \times 2.5 \text{ cm}^2$ geometric electrode surface area, thickness 1 mm) at a distance of about 3 mm are used as the electrodes. Under ultrasonic action, a current of 5 mA which is increased to 15 mA in the course of 20 minutes is passed between the nickel electrodes. By means of jacket cooling, the electrolytic cell is maintained at 16°C. In the course of the electrolysis, the electrolyte turns deep-black. After 320 C have been passed, the electrolysis is stopped and the electrolyte is pressed into a 150 ml nitrogenized vessel. During this period, 89 mg of Ni have dissolved anodically, corresponding to a current efficiency of 96% with an uptake by nickel of 2 electrons. Evaporation of the solvent under oil pump vacuum yields 5 g of a black viscous mass. Addition of 30 ml of an ether/ethanol mixture (9/1) results in the formation of a grey-black precipitate upon vigorous shaking. The latter is allowed to set for 24 hours, whereupon the clear supernatant is syphoned off. Washing is performed with 10 ml of pentane, and after drying under oil pump vacuum for 20 minutes, 178 mg (80% yield based on Ni dissolved) of a grey-black powder is obtained. This powder readily dissolves in THF and toluene, and is insoluble in diethyl ether, acetonitrile, and pentane. The colloid is very sensitive to air and moisture. Elemental analysis: Ni: 36.46%; C: 28.29%; H: 4.01%; N: 13.22%; Br: 2.72%.

Transmission electron micrographs show a narrow size distribution of colloids which are all ≤ 6 nm in diameter and have spherical geometries.

Example 17: (Pt)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 60 ml of 0.2 M tetrabutylammonium bromide in ACN. All operations must be performed under an inert gas atmosphere (argon or nitrogen). Two sheets of pure platinum ($2 \times 2.5 \text{ cm}^2$ geometric electrode surface area, thickness 1 mm) at a distance of about 3 mm are used as the electrodes. Under ultrasonic action, a current of 30 mA which is increased to 100 mA in the course of 20 minutes is passed between the platinum electrodes. By means of jacket cooling, the electrolytic cell is maintained at 30°C. In the course of the electrolysis, the electrolyte turns deep-black. After 3200 C have been passed, the electrolysis is stopped and the electrolyte is pressed into a 150 ml nitrogenized vessel. During this period, 330 mg of Pt have dissolved anodically, corresponding to a current efficiency of 10% with an uptake by platinum of 2 electrons. Addition of 30 ml of oxygen-free water results in the formation of a grey-black precipitate upon vigorous shaking. The latter is allowed to set for 24 hours, whereupon the clear supernatant is syphoned off. Drying under oil pump vacuum yields 410 mg of a grey-black powder which is amorphous by X-ray diffraction. It very readily dissolves in ACN and DMF, and is insoluble in THF, diethyl ether, pentane, water, and toluene.

Elemental analysis: 80% of Pt

Transmission electron micrographs show a narrow size distribution of Pt colloids in a size range of ≤ 2 nm.

Example 18: (Rh)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 60 ml of 0.2 M tetrabutylammonium chloride in ACN. All operations must be performed under an inert gas atmosphere (argon or nitrogen). Two sheets of pure rhodium ($2 \times 2.5 \text{ cm}^2$ geometric electrode surface area, thickness 1 mm) at a distance of about 3 mm are used as the electrodes. Under ultrasonic action, a current of 20 mA which is increased to 75 mA in the course of 20 minutes is passed between the rhodium electrodes. By means of jacket cooling, the electrolytic cell is maintained at 30°C. In the course of the electrolysis, the electrolyte

vacuum yields 5 g of a black viscous mass. Addition of 30 ml of an ether/ethanol mixture (9/1) results in the formation of a grey-black precipitate upon vigorous shaking. The latter is allowed to set for 24 hours, whereupon the clear supernatant is syphoned off. Washing is performed with 10 ml of pentane, and after drying under oil pump vacuum for 20 minutes, 178 mg (80% yield based on Ni dissolved) of a grey-black powder is obtained. This powder readily dissolves in THF and toluene, and is insoluble in diethyl ether, acetonitrile, and pentane. The colloid is very sensitive to air and moisture.

Elemental analysis: 60% of Ni

Transmission electron micrographs show a broader size distribution of colloids which are all < 30 nm in diameter and have spherical or polyhedral geometries. The colloid particles are significantly larger than those in example 16 where a lower current density has been employed (cf. examples 2 through 4: Pd).

Example 22: (Ag)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 90 ml of 0.1 M tetraoctylammonium bromide in THF. All operations must be performed under an inert gas atmosphere (argon or nitrogen). Two sheets of fine silver (2 x 2.5 cm² geometric electrode surface area, thickness 1 mm) at a distance of about 3 mm are used as the electrodes. Under ultrasonic action, a current of 5 mA which is increased to 15 mA in the course of 20 minutes is passed between the silver electrodes. By means of jacket cooling, the electrolytic cell is maintained at 16 °C. In the course of the electrolysis, the electrolyte turns deep-cherry to black. After 640 C have been passed, the electrolysis is stopped and the electrolyte is pressed into a 150 ml nitrogenized vessel. During this period, 712 mg of Ag have dissolved anodically, corresponding to a current efficiency of 96% with an uptake by silver of 1 electron. Evaporation of the solvent under oil pump vacuum leaves 700 mg of a black viscous mass. The colloid is sensitive to air and moisture. The nanocrystalline powder thus obtained is not redispersible in THF.

Elemental analysis of the powder: 93% of Ag

Transmission electron micrographs show a narrow size distribution of agglomerated particles which are all ≤ 12 nm in diameter and have spherical or hexagonal geometries.

Example 23: (Pd/Ni)

Experimental protocol for the preparation of a Pd/Ni bimetallic colloid

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 80 ml of 0.1 M tetraoctylammonium bromide in THF. A sheet of pure platinum (5 x 5 cm² geometric electrode surface area) is used as the cathode. An electrode of pure nickel and an electrode of pure palladium (2.5 x 5 cm² geometric electrode surface area) which are placed side by side at a distance of 4 mm to the cathode are both used as anodes. All operations must be performed under an inert gas atmosphere (argon); all solvents must be thoroughly dried and freshly distilled. At a temperature of 30 °C and under ultrasonic action, a current of 30 mA is passed between nickel and platinum as well as between palladium and platinum by means of a double power supply unit, so both currents can be controlled independently. In the course of the electrolysis, the solution turns deep-brown to black. After a total of 1 Ah has been passed, the electrolysis is stopped. During this period, 350 mg of nickel (= 65% current efficiency) and 600 mg of palladium (= 61% current efficiency) have dissolved. The solvent is evaporated and the tacky residue is dried under a good oil pump vacuum. The black residue thus obtained is washed first with 50 ml of pentane and thereafter 5 times with 40 ml of an ethanol/pentane mixture (1.5/10). After drying under oil pump vacuum, 1.1 g of a grey-black powder is obtained. This powder very readily dissolves in THF and acetone, is less soluble in toluene and ethanol, and insoluble in ether, pentane, acetonitrile, and water.

The THF colloid solutions thus obtained are stable for months.

Transmission electron micrographs show well-separated, spherically shaped colloids in a size range of from 0.5 to 4 nm. Energy-dispersive X-ray spot analyses (EDX) reveal that almost all of the colloid particles contain both metals. Investigations by elemental analysis indicate a Pd/Ni ratio of 42/18.

Example 24:

Experimental protocol for the preparation of a Pd/Ni bimetallic colloid

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 80 ml of 0.1 M tetraoctylammonium bromide in THF. A sheet of pure platinum (5 x 5 cm² geometric electrode surface area) is used as

water and acetone.

Elemental analysis: 58.8% of Pd; the residual 41.2% consists of tetraoctadecylammonium bromide protecting the particles as a colloid stabilizer.

Transmission electron micrographs show a narrow size distribution of colloids which are all ≤ 6 nm in diameter and have spherical geometries. The solubilities of the colloid powders depend on the protective colloid employed and can be adjusted within a selected range from water soluble to pentane soluble:

protective colloid employed	solubility of colloid powder	Example No.
(dimethyldodecylammonio)propanesulfonate	water > ethanol	8
tetrabutylammonium bromide	DMF \gg THF	10
tetrabutylammonium bromide	THF > toluene	1
tetradodecylammonium bromide	toluene > THF	9
tetraoctadecylammonium bromide	pentane > toluene \gg THF	26

Example 27: (Pd)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 90 ml of 0.1 M tetraoctylammonium perchlorate in THF. All operations must be performed under an inert gas atmosphere (argon or nitrogen). Two sheets of pure palladium (2×2.5 cm² geometric electrode surface area, thickness 1 mm) at a distance of about 3 mm are used as the electrodes. With vigorous stirring or with the use of ultrasonic waves, a current of 5 mA which is increased to 17 mA in the course of 20 min is passed between the palladium electrodes. By means of jacket cooling, the electrolytic cell is maintained at 16 °C. In the course of the electrolysis, the electrolyte turns deep-black and a grey-brown powder precipitates. After a charge of 640 C has been passed, the electrolysis is stopped and the electrolyte is pressed into a 150 ml nitrogenized vessel. During this period, 300 mg of palladium have dissolved anodically, corresponding to an anodic efficiency of 90%. The precipitate is allowed to set for 24 hours, whereupon the brown supernatant is syphoned off. After drying under oil pump vacuum for 20 minutes, 320 mg of a grey-black solid is obtained which consists of agglomerated Pd particles having sizes of ≤ 8 nm according to transmission electron micrographs. Elemental analysis indicates a Pd content of 92% (the remainder is tetraoctylammonium perchlorate). The powder thus obtained is not completely soluble in THF or other solvents, however, which indicates poor wetting of the colloid particles by the stabilizer. The same results have been obtained with other large, non-coordinating anions, such as BF₄⁻. Coordinating anions, such as e.g. halogenide, are crucial to the stabilization of the colloids and hence redispersibility.

Example 28: (Pd)

Preparation of a colloid with chiral protective shell - chirality at the quaternary N atom

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 90 ml of 0.1 M butylbenzylododecylammonium bromide in THF. Two sheets of pure palladium (2×2.5 cm² geometric electrode surface area, thickness 1 mm) at a distance of about 3 mm are used as the electrodes. All operations must be performed under an inert gas atmosphere (argon or nitrogen). With vigorous stirring by means of a magnetic stirrer or with the use of ultrasonic waves, a current of 5 mA which is increased to 17 mA in the course of 10 min is passed between the palladium electrodes. By means of a jacket heating, the electrolytic cell is maintained at 30 °C. In the course of the electrolysis, the electrolyte turns deep-black. After a charge of 640 C has been passed, the electrolysis is stopped and the electrolyte is pressed into a 150 ml nitrogenized vessel. During this period, 300 mg of palladium have dissolved anodically, corresponding to an anodic efficiency of 90%. Addition of 25 ml of oxygen-free water results in the formation of a brown-grey precipitate. This is allowed to set for 24 hours, whereupon the clear supernatant is syphoned off. After drying under oil pump vacuum, 350 mg of a grey-black solid is obtained. This solid readily dissolves in THF and toluene, and is insoluble in water and pentane.

Elemental analysis: 72% of Pd; the residual 28% consists of butylbenzylododecylammonium bromide protecting the particles as a colloid stabilizer.

- Elemental analysis: 51% of platinum. The remainder consists of the ammonium salt. This corresponds to an efficiency of 90% with an uptake of 2 electrons per platinum ion. Transmission electron micrographs show a narrow size distribution of colloids which are all 3-5 nm in diameter and have spherical geometries. Comparative TEM/STM investigations of these colloids (adsorbed from a DMF solution, substrate 200 nm gold on Tempax quartz carrier) clearly show coating of the metal cores with a monomolecular layer of stabilizer. Electrolyses with PtBr_2 , PtI_2 , and platinum(II) acetylacetonate proceed in much the same way.

Example 32: (Pt)

- The procedure and processing are analogous to that of Example 31. Electrolyte: 100 ml of 0.1 M tetrabutylammonium acetate in THF/ACN (4/1). Metal salt: 0.5 g of PdCl_2 . Current: 5 mA, increased to 20 mA in the course of 10 minutes. Charge passed: 500 C. Product: 440 mg of a grey-black powder. This powder readily dissolves in DMF, and is insoluble in water, diethyl ether, THF, acetonitrile, toluene, and pentane.
- Elemental analysis: 62% of palladium. Yield 93%. Size: < 5 nm. Electrolyses with PdBr_2 , PdI_2 , and palladium(II) acetylacetonate proceed in much the same way.

Example 33: (Pd)

- The procedure and processing are analogous to that of Example 31. Electrolyte: 100 ml of 0.1 M tetrabutylammonium trifluoroacetate in THF. Metal salt: 0.5 g of PdCl_2 . Charge passed: 500 C. Product: 458 mg of a grey-black powder. This powder readily dissolves in DMF, and is insoluble in water, diethyl ether, THF, acetonitrile, toluene, and pentane.
- Elemental analysis: 54% of palladium. Yield 84%. Diameter < 5 nm. Electrolyses with PdBr_2 , PdI_2 , and palladium(II) acetylacetonate proceed in much the same way.

Example 34: (Mo)

- The procedure and processing are analogous to that of Example 31. Electrolyte: 50 ml of 0.1 M tetraoctylammonium bromide in THF. Metal salt: 50 ml of 0.05 M $\text{Mo}_2(\text{OAc})_4$ in THF. Charge passed: 480 C. The electrolyte is pressed into a 200 ml nitrogenized vessel and addition of 20 ml of diethyl ether results in the formation of a grey-black precipitate upon vigorous shaking. Product: 265 mg of a black powder. This powder readily dissolves in THF and toluene, and is insoluble in water, diethyl ether, DMF, acetonitrile, and pentane.
- Elemental analysis: 37% of molybdenum. Yield 72%. Diameter: 1-5 nm. Electrolyses with Noct_4Cl , $\text{Noct}_4\text{ClO}_4$, Noct_4PF_6 , Noct_4BF_4 , Noct_4OTf , Noct_4OTs , Poct_4Cl , or Poct_4Br as the stabilizer proceed in much the same way.

Example 35: (Rh)

- The procedure and processing are analogous to that of Example 31. Electrolyte: 50 ml of 0.1 M tetrabutylammonium acetate in THF, and 50 ml of 0.1 M tetrabutylammonium chloride in THF. Metal salt: 0.5 g of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$. Charge passed: 700 C. Product: 440 mg of a grey-black powder. This powder readily dissolves in DMF, and is insoluble in water, diethyl ether, THF, acetonitrile, toluene, and pentane.
- Elemental analysis: 46% of rhodium. Yield: 92%. Diameter: 2-3 nm. Electrolyses with $\text{RhBr}_3 \cdot x\text{H}_2\text{O}$ and RhCl_3 proceed in much the same way.

Example 36: (Ru)

- The procedure and processing are analogous to that of Example 31. Two sheets of pure platinum (4 x 4 cm^2 geometric electrode surface area, thickness 0.5 mm) at a distance of about 3 mm are used as the electrodes. Metal salt: 0.5 g of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$. By means of jacket cooling, the electrolytic cell is maintained at 18°C. Charge passed: 650 C. Within 24 hours, a grey-black precipitate forms. Product: 290 mg of a grey-black powder. This powder readily dissolves in DMF, and is insoluble in water, diethyl ether, THF, acetonitrile, toluene, and pentane.
- Elemental analysis: 55% of ruthenium. Yield: 73%. Diameter: < 5 nm. Electrolyses with RuCl_3 proceed in much the same way.

a current of 2 mA which is increased to 20 mA in the course of 10 min is passed between the platinum electrodes. By means of jacket cooling, the electrolytic cell is maintained at 20°C. In the course of the electrolysis, the electrolyte turns deep-black. After a charge of 600 C has been passed, the electrolysis is stopped and the electrolyte is pressed into a 200 ml nitrogenized vessel. Addition of 15 ml of oxygen-free water to the electrolyte results in the formation of a grey-black precipitate upon vigorous shaking. After 24 hours, the slightly brown clear supernatant is pressed off under inert gas and the precipitate is washed twice with 10 ml of diethyl ether. Drying under oil pump vacuum for 24 hours yields 380 mg of a black powder. This powder readily dissolves in THF and toluene, and is insoluble in water, diethyl ether, DMF, acetonitrile, and pentane.

Elemental analysis: 55% of indium. This corresponds to an efficiency of 89% with an uptake of 3 electrons per indium ion. Transmission electron micrographs show a size distribution of colloids which are all < 10 nm in diameter and have spherical geometries. Electrolyses with Noct_4Cl , $\text{Noct}_4\text{ClO}_4$, Noct_4PF_6 , Noct_4BF_4 , Noct_4OTf , Noct_4OTs , Poct_4Cl , or Poct_4Br as the stabilizer proceed in much the same way.

Example 43:

(Ti)

The procedure and processing are analogous to that of Example 31. Metal salt: 0.5 g of $\text{Ti}(\text{OAc})_3$. Charge passed: 370 C. Product: 530 mg of a black powder. This powder readily dissolves in DMF, and is insoluble in water, THF, diethyl ether, toluene, acetonitrile, and pentane.

Elemental analysis: 36% of thallium. Yield: 72%. Diameter: 1-5 nm.

Example 44:

(Pd)

The procedure and processing are analogous to that of Example 42. Metal salt: 0.5 g of $\text{Pd}(\text{OAc})_2$. Charge passed: 430 C. Product: 288 mg of a black powder. This powder readily dissolves in THF and toluene, and is insoluble in water, diethyl ether, DMF, acetonitrile, and pentane.

Elemental analysis: 72% of palladium. Yield: 88%. Diameter: 3-4 nm. Comparative TEM/STM investigations of these colloids (adsorbed from a THF solution, substrate: 200 nm gold on Tempax quartz carrier) clearly show coating of the metal cores with a monomolecular layer of stabilizer. Electrolyses with Noct_4Cl , $\text{Noct}_4\text{ClO}_4$, Noct_4PF_6 , Noct_4BF_4 , Noct_4OTf , Noct_4OTs , Poct_4Cl , or Poct_4Br as the stabilizer proceed in much the same way.

Example 45:

(Pt)

The procedure and processing are analogous to that of Example 42. Electrolyte: 100 ml of 0.1 M tetraoctylammonium bromide in THF/water (10/1). Metal salt: 0.5 g of PtBr_2 . Charge passed: 270 C. Product: 420 mg of a black powder. This powder readily dissolves in THF and toluene, and is insoluble in water, diethyl ether, DMF, acetonitrile, and pentane.

Elemental analysis: 41% of platinum. Yield: 63%. Diameter: 1-10 nm. Electrolyses with Noct_4Cl , $\text{Noct}_4\text{ClO}_4$, Noct_4PF_6 , Noct_4BF_4 , Noct_4OTf , Noct_4OTs , Poct_4Cl , or Poct_4Br as the stabilizer proceed in much the same way.

Example 46:

(Pd)

The procedure and processing are analogous to that of Example 31. Electrolyte: 100 ml of 0.1 M tetrabutylammonium bromide in THF. Metal salt: 0.5 g of $\text{Pd}(\text{OAc})_2$. Charge passed: 430 C. Product: 294 mg of a black powder. This powder very readily dissolves in DMF, and is insoluble in water, diethyl ether, THF, acetonitrile, toluene, and pentane.

Elemental analysis: 71% of palladium. Yield: 89%. Diameter: 3-4 nm. Comparative TEM/STM investigations of these colloids (adsorbed from a DMF solution, substrate: 200 nm gold on Tempax quartz carrier) clearly show coating of the metal cores with a monomolecular layer of stabilizer. Electrolyses with NBu_4Cl , NBu_4I , NBu_4ClO_4 , NBu_4PF_6 , NBu_4BF_4 , NBu_4OTf , NBu_4OTs , PBu_4Cl , or PBu_4Br as the stabilizer proceed in much the same way.

Example 47:

(Pd)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 100 ml of 0.1 M tetraoctadecylammonium bromide in THF, thermostated at 60°C. Two sheets of pure platinum ($1.5 \times 2 \text{ cm}^2$

Example 52: (Pd)

The procedure and processing are analogous to that of Example 31. Electrolyte: 100 ml of 0.1 M 3-(dimethyldodecylammonio)propanesulfonate • LiCl in THF. Metal salt: 0.5 g of Pd(OAc)₂. Current: 2 mA, increased to 15 mA in the course of 10 minutes. By means of jacket cooling, the electrolytic cell is maintained at 40 °C. Charge passed: 430 C. Product: 402 mg of a grey-black powder. This powder readily dissolves in water, methanol and ethanol, and is insoluble in THF, toluene, diethyl ether, DMF, acetonitrile, and pentane.

Elemental analysis: 52% of palladium. Yield: 89%. Diameter: 1-10 nm. Electrolyses with 3-(N,N-dimethylstearyl ammonio)propane-sulfonate as the stabilizer proceed in much the same way. Comparative TEM/STM investigations of these colloids (adsorbed from an aqueous solution, substrate: 200 nm gold on Tempax quartz carrier) clearly show coating of the metal cores with a monomolecular layer of stabilizer. Survey of the solubilities of differently stabilized colloids:

Example	stabilizer	colloid is soluble in
52	(dimethyldodecylammonio)propanesulfonate	water > ethanol
31	tetrabutylammonium ...	DMF >> THF
34	tetraoctylammonium ...	THF > toluene
47	tetraoctadecylammonium ...	pentane > toluene >> THF

Example 53: (Ru)

The procedure and processing are analogous to that of Example 52. Electrolyte: 100 ml of 0.1 M 3-(dimethyldodecylammonio)propanesulfonate • LiOAc in THF. Metal salt: 0.5 g of RuCl₃ • H₂O. Charge passed: 650 C. Product: 270 mg of a black powder. This powder very readily dissolves in water, and is insoluble in DMF, diethyl ether, THF, acetonitrile, toluene, and pentane.

Elemental analysis: 58% of ruthenium. Yield: 75%. Diameter: 1-2 nm. Comparative TEM/STM investigations of these colloids (adsorbed from an aqueous solution, substrate: 200 nm gold on Tempax quartz carrier) clearly show coating of the metal cores with a monomolecular layer of stabilizer.

Example 54: (Pd)

The procedure and processing are analogous to that of Example 31. Electrolyte: 100 ml of 0.05 M tetrabutylammonium bromide in propylene carbonate. Metal salt: 0.5 g of Pd(OAc)₂. Charge passed: 430 C. Product: 550 mg of a black powder. This powder very readily dissolves in DMF, and is insoluble in water, diethyl ether, THF, acetonitrile, toluene, and pentane.

Elemental analysis: 41% of palladium. Yield: 96%. Diameter: 1-5 nm. Electrolyses with NBu₄Cl, NBu₄I, NBu₄ClO₄, NBu₄PF₆, NBu₄BF₄, NBu₄OTf, NBu₄OTs, PBu₄Cl, or PBu₄Br as the stabilizer proceed in much the same way.

Example 55: (Pd)

The procedure and processing are analogous to that of Example 31. Electrolyte: 100 ml of 0.05 M tetrabutylammonium bromide in acetonitrile. Metal salt: 0.5 g of Pd(OAc)₂. Charge passed: 430 C. Product: 367 mg of a black powder. This powder very readily dissolves in DMF, and is insoluble in water, diethyl ether, THF, acetonitrile, toluene, and pentane.

Elemental analysis: 57% of palladium. Yield: 89%. Diameter: 1-5 nm. Electrolyses with NBu₄Cl, NBu₄I, NBu₄ClO₄, NBu₄PF₆, NBu₄BF₄, NBu₄OTf, NBu₄OTs, PBu₄Cl, or PBu₄Br as the stabilizer proceed in much the same way.

Example 56: (Pt)

The procedure and processing are analogous to that of Example 31. Two sheets of pure platinum (4 x 4 cm² geometric electrode surface area, thickness 0.5 mm) at a distance of about 3 mm are used as the electrodes. Current: 1 mA. Product: 630 mg of a grey-black powder. This powder readily dissolves in DMF, and is insoluble in water, diethyl ether, THF, acetonitrile, toluene, and pentane.

Elemental analysis: 12% of palladium. The powder thus prepared is very useful for the preparation of films and workpieces. Embeddings using PMMA and polystyrene proceed in much the same way.

Example 61: (Rh)

The procedure and processing are analogous to that of Example 31. Metal salts: 0.25 g of PtCl_2 and 0.25 g of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. Charge passed: 530 C. Product: 360 mg of a grey-black powder. This powder readily dissolves in DMF, and is insoluble in water, diethyl ether, THF, acetonitrile, toluene, and pentane.

Elemental analysis: 42% of platinum and 24% of rhodium. Yield: 86%. Diameter: < 3 nm. Energy-dispersive X-ray spot analysis (EDX) of individual particles clearly shows that both platinum and rhodium are present in the colloids. Comparative TEM/STM investigations of these colloids (adsorbed from a DMF solution, substrate: 200 nm gold on Tempax quartz carrier) clearly show coating of the metal cores with a monomolecular layer of stabilizer. Electrolyses of platinum from PtBr_2 , PtI_2 , platinum(II) acetylacetonate, and of rhodium from RhCl_3 and $\text{RhBr}_3 \cdot x\text{H}_2\text{O}$ proceed in much the same way.

Example 62: (Rh)

The procedure and processing are analogous to that of Example 31. Metal salts: 450 mg of PtCl_2 and 50 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. Charge passed: 400 C. Product: 340 mg of a grey-black powder. This powder readily dissolves in DMF, and is insoluble in water, diethyl ether, THF, acetonitrile, toluene, and pentane.

Elemental analysis: 62% of platinum and 4% of rhodium. Yield: 83%. Diameter: < 3 nm. Energy-dispersive X-ray spot analysis (EDX) of individual particles clearly shows that both platinum and rhodium are present in the colloids. Electrolyses of platinum from PtBr_2 , PtI_2 , platinum(II) acetylacetonate, and of rhodium from RhCl_3 and $\text{RhBr}_3 \cdot x\text{H}_2\text{O}$ proceed in much the same way.

Example 63: (PdCu)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte are charged 100 ml of 0.1 M tetraoctylammonium bromide in THF. The following serve as electrodes: a sheet of pure platinum is used as the cathode and a sheet of pure copper is used as the anode (1.5 x 2 cm² geometric electrode surface area, thickness 0.5 mm) at a distance of about 3 mm. All operations must be performed under an inert gas atmosphere (argon or nitrogen). Under ultrasonic action, 0.5 g of PdBr_2 is dissolved in the electrolyte and a current of 2 mA which is increased to 20 mA in the course of 10 minutes is passed between the electrodes. By means of jacket cooling, the electrolytic cell is maintained at 20 °C. In the course of the electrolysis, the electrolyte turns deep-black. After a charge of 490 C has been passed, the electrolysis is stopped and the electrolyte is pressed into a 200 ml nitrogenized vessel. Addition of 15 ml of oxygen-free water to the electrolyte results in the formation of a grey-black precipitate upon vigorous shaking. After 24 hours, the slightly brown clear supernatant is pressed off under inert gas and the precipitate is washed twice with 10 ml of diethyl ether. Drying under oil pump vacuum for 24 hours yields 570 mg of a black powder. This powder readily dissolves in THF and toluene, and is insoluble in water, diethyl ether, DMF, acetonitrile, and pentane.

Elemental analysis: 35% of palladium and 15% of copper. The remainder is the tetraoctylammonium bromide stabilizer. This corresponds to an efficiency of 97%. Transmission electron micrographs show a size distribution of colloids which are all 1-5 nm in diameter and have spherical geometries. Energy-dispersive X-ray spot analysis (EDX) of individual particles clearly shows that both palladium and copper are present in the colloids. Electrolyses with Noct_4Cl , $\text{Noct}_4\text{ClO}_4$, Noct_4PF_6 , Noct_4BF_4 , Noct_4OTf , Noct_4OTs , Poct_4Cl , or Poct_4Br as the stabilizer proceed in much the same way.

Example 64: (PdCu)

The procedure and processing are analogous to that of Example 63. Metal salt: 0.5 g of PtCl_2 . Charge passed: 495 C. Product: 675 mg of a black powder. This powder readily dissolves in THF and toluene, and is insoluble in water, diethyl ether, DMF, acetonitrile, and pentane.

Elemental analysis: 53% of platinum and 23% of copper. Yield: 98%. Diameter: 1-5 nm. Energy-dispersive X-ray spot analysis (EDX) of individual particles clearly shows that both platinum and copper are present in the colloids. Electrolyses with Noct_4Cl , $\text{Noct}_4\text{ClO}_4$, Noct_4PF_6 , Noct_4BF_4 , Noct_4OTf , Noct_4OTs , Poct_4Cl , or Poct_4Br as the stabilizer proceed in much the same way.

Example 70: (Pd)

In a multi-purpose electrolytic cell for 20-100 ml of electrolyte, 10 mg of palladium colloid (cf. Example 32, metal content 62%) is dissolved in 20 ml of DMF. As electrodes, a sheet of pure platinum is used as the cathode and a piece of freshly drawn graphite (HOPG) is used as the anode (1 x 1 cm² geometric electrode surface area) at a distance of about 6 mm. All operations must be performed under an inert gas atmosphere (argon or nitrogen). For 30 seconds, a voltage of 30 volts is applied between the electrodes. Subsequently, the graphite electrode is removed and washed twice with 3 ml of diethyl ether.

Scanning force microscopic studies clearly show covering of the surface with the colloid.

Example 71: (Pd)

In a 2 ml plastic vessel, 160 μ l of 0.1 M aqueous sodium fluoride is added with stirring to 4 mmol of Mg(OEt)₂, 1 mmol of methyl-trimethoxysilane, 1 mg of palladium colloid (metal content 44%), and 200 μ l of THF. After drying at 50 °C for 24 hours, remaining volatile components are removed under oil pump vacuum for another 24 hours. Then, the mortar-ground residue in ethanol is refluxed for 24 hours. After decantation, the solid is dried under oil pump vacuum. Elemental analysis: 0.1% of palladium.

Example 72: (Pd)

In a 60 ml miniautoclave, 85 mg of palladium in sol-gel matrix (cf. Example 71, metal content 0.1%) are suspended in 20 ml of DMF. After 2 mmol of iodobenzene, 2 mmol of styrene, and 4 mmol of tetrabutylammonium acetate have been added, heating at 60 °C is performed with shaking. After 12 h, 288 mg of stilbene can be isolated from the reaction solution. This corresponds to an 80% yield.

Example 73: (Pt)

The procedure and processing are analogous to that of Example 31. Two sheets of pure platinum (4 x 4 cm² geometric electrode surface area, thickness 0.5 mm) at a distance of about 3 mm are used as the electrodes. Metal salt: 0.5 g of YCl₃. By means of jacket cooling, the electrolytic cell is maintained at 18 °C. Charge passed: 750 C. Within 24 hours, a grey-black precipitate forms. Product: 420 mg of a grey-black powder. This powder readily dissolves in DMF, and is insoluble in diethyl ether, THF, acetonitrile, toluene, and pentane.

Elemental analysis: 22% of yttrium. Yield: 40%. Diameter: < 5 nm.

Example 74: (Zr)

The procedure and processing are analogous to that of Example 31. Two sheets of pure platinum (4 x 4 cm² geometric electrode surface area, thickness 0.5 mm) at a distance of about 3 mm are used as the electrodes. Metal salt: 0.5 g of ZrCl₄. By means of jacket cooling, the electrolytic cell is maintained at 18 °C. Charge passed: 825 C. Within 24 hours, a grey-black precipitate forms. Product: 244 mg of a grey-black powder. This powder readily dissolves in DMF, and is insoluble in diethyl ether, THF, acetonitrile, toluene, and pentane.

Elemental analysis: 36% of zirconium. Yield: 45%. Diameter: < 3 nm.

Example 75: (Nb)

The procedure and processing are analogous to that of Example 31. Two sheets of pure platinum (4 x 4 cm² geometric electrode surface area, thickness 0.5 mm) at a distance of about 3 mm are used as the electrodes. Metal salt: 0.5 g of NbBr₅. By means of jacket cooling, the electrolytic cell is maintained at 18 °C. Charge passed: 500 C. Within 24 hours, a grey-black precipitate forms. Product: 114 mg of a grey-black powder. This powder readily dissolves in DMF, and is insoluble in water, diethyl ether, THF, acetonitrile, toluene, and pentane.

Elemental analysis: 50% of niobium. Yield: 60%. Diameter: 1-3 nm.

Elemental analysis: 39 % palladium. Transmission electron micrographs show a narrow size distribution of colloids which are all < 10 nm in diameter.

Example 82: (Pt)

The procedure and processings are analogous to that of Example 81. Metal salt: 0.5 g PtCl_2 . Charge passed: 365 C. The solvent is evaporated under oil pump vacuum and the residue is washed twice with a mixture of ethanol/ether (1:10). Drying under oil pump vacuum for 24 hours yields 720 mg of a light-grey powder.

Elemental analysis: 46 % platinum. Transmission electron micrographs show a narrow size distribution of colloids which are all < 10 nm diameter.

Example 83: (Pd)

In a 150 ml vessel, 100 mg of palladium colloid (cf. Example 52, metal content 57 %, average size 3-5 nm) is dissolved in 100 ml of water. With vigorous stirring 5.0 g mortar ground alumina is added and stirring is continued for another 3 hours. After 30 min the colorless supernatant is syphoned off. Drying under oil pump vacuum for 24 hours yields 5.1 g of a light-grey powder.

Elemental analysis: 1.1 % palladium. Transmission electron micrographs show a narrow size distribution of colloids which are all 3-5 nm in diameter, have spherical geometries and are individually fixed on the substrate. These supported palladium clusters are embedded in carbon by means of glow evaporation. Ultramicrotome sections of this material show that the metal colloid is only on the surface of the alumina grains.

Example 84: (Pd)

In a 150 ml vessel, 150 mg of palladium colloid (cf. Example 52, metal content 57 %, average size 3-5 nm) is dissolved in 100 ml of water. With vigorous stirring 3.0 g mortar ground carbon black (Vulcan® XC-72) is added and stirring is continued for another 3 hours. After 30 min the colorless supernatant is syphoned off. Drying under oil pump vacuum for 24 hours yields 3.15 g of a black powder.

Elemental analysis: 2.7 % palladium. Transmission electron micrographs show a narrow size distribution of colloids which are all 3-5 nm in diameter, have spherical geometries and are individually fixed on the substrate. Thus, the same size distribution as prior to substrate fixation is observed. Substrate fixations using Al_2O_3 , TiO_2 , SiO_2 , La_2O_3 , Y_2O_3 , MgO or Kevlar® as the substrate material proceed in much the same way.

Example 85: (Pd)

In a 50 ml vessel, 15 mg of palladium colloid (cf. Example 52, metal content 57 %, average size 3-5 nm) is dissolved in 100 ml of water. With, vigorous shaking 250 mg Bioran® controlled pore glas (pore diameter 101 nm, particle size 130-250 μm) is added and shaking is continued for another 3 hours. After 30 min the colorless supernatant is filtered off. Drying of the residue under oil pump vacuum for 24 hours yields 264 mg of a grey material.

Elemental analysis: 3.2 % palladium. Transmission electron micrographs show a narrow size distribution of colloids which are all 3-5 nm in diameter, have spherical geometries and are individually fixed on the substrate. Thus, the same size distribution as prior to substrate fixation is observed. Substrate fixations using Siran® as the substrate material proceed in much the same way.

Claims

1. A method for the electrochemical preparation of metal colloids with particle sizes of less than 30 nm, characterized in that one or more metals of groups Ib, IIb, III, IV, V, VI, VIIb, VIII, lanthanoides, and/or actinoides of the periodic table are cathodically reduced in the presence of a stabilizer, optionally with a supporting electrolyte being added, in organic solvents or in solvent mixtures of organic solvents and/or water within a temperature range of between -78°C and $+120^\circ\text{C}$ to form metal colloidal solutions or redispersible metal colloid powders, optionally in the presence of inert substrates and/or soluble metal salts of the respective metals.

18. Watersoluble metal colloids, bimetallic colloids or multi-metallic colloids comprising metals of groups Ib, IIb, III, IV, V, VI, VIIb, VIII, lanthanoides, and/or actinoides of the periodic table and having particle sizes of up to 30 nm stabilized by the presence of watersoluble, in particular cationic, anionic, betainic or nonionic stabilizers.

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19. Inert substrates selected in particular from carbon blacks, active charcoal, glasses, inorganic oxides and organic polymers coated with metal colloids according to claims 17 or 18.

20. Substrates according to claim 19, characterized in that the surface of the substrates is coated with a monomolecular, bimolecular or multimolecular layer of the colloids.

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21. Use of the coated substrates according to claims 19 or 20 as such or after the removal of the stabilizer as catalyst in the organic synthesis.

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